THE SEARCH FOR WATER AND OTHER VOLATILE-BEARING PHASES ON MARS: MAUNA KEA VOLCANO AS AN ANALOG: ¹D. W. Ming*, ²H. V. Lauer, Jr., ²D. C. Golden, and ¹R. V. Morris; ¹ARES, NASA Johnson Space Center, ²Houston, TX; Lockheed Martin, Houston, TX (*e-mail: douglas.w.ming1@jsc.nasa.gov)

Introduction: The theme of NASA's Mars Exploration Program is to "follow the water," which has important implications in the search for life, climate evolution, evolution of the Martian surface and interior, and preparing for human exploration. The two Viking Landers detected small amounts of water (e.g., 1-2 wt. %) in the surface materials. However, it is not known how the water is incorporated into these materials. From Viking data, it appears that most of the water evolved between 350 and 500°C. It was difficult to interpret the water data in terms of mineralogy because of the uncertainty of the Viking GC-MS measurements; the large temperature increases between evolved gas analysis (i.e., 150°C steps, which precludes obtaining an accurate temperature for evolution of water), and the large number of candidate minerals that may evolve water in this temperature range. Biemann et al. [1] suggested that candidate Viking landing site minerals might include phyllosilicates, goethite, and hydrated sulfates. Recent results from Mars Odyssey's neutron and gamma ray spectrometers suggest significant amounts of water ice near the surface at high latitudes and higher than expected water contents in near-equatorial and midlatitude regions [2,3]. However, it is not clear how water is bound in regolith materials.

Thermal and evolved gas analysis of volatile-bearing materials is a powerful method to identify and characterize the volatile phases in Mars surface materials. Unfortunately, the Thermal Evolved Gas Analyzer (TEGA) was unable to characterize volatile-bearing phases when the Mars Polar Lander was lost. However, future missions will have the opportunity to characterize volatile-bearing phases, i.e., Beagle 2, 2007 Mars Scout, and 2009 Mars Science Laboratory.

Over the past 5 years, we have conducted field studies on the summit cones of Mauna Kea Volcano in Hawaii. Basaltic materials on several of these summit cones (i.e., Puu Poliahu, Puu Waiau) have been significantly altered by hydrothermal activity [4], whereas other summit cones have not undergone extensive aqueous alteration. These summit cones provide an important environment to study analogs of Martian surface alteration materials and analog surface processes (i.e., hydrothermal alteration, palagonitization [e.g., 5,6]).

In on-going research, we have characterized the thermal and evolved gas behaviors of volatile-bearing reference minerals at reduced pressures in support of TEGA [7]. We have expanded those studies to characterize the thermal and evolved gas behaviors of Mauna Kea samples as an analog for Mars surface materials. These samples were chosen for two reasons. First, many have chemical and spectral properties similar to what we see from remote sensing data from the Martian surface [e.g., 5,6,8]. Second, these samples have a range of mineralogical and chemical properties, ranging from simple to very complex; hence it will be challenging to characterize their thermal and evolved gas behaviors and to provide a context for their geological evolution. However, these types of studies are absolutely critical to understanding relevant geologic processes on Mars during robotic missions to the surface.

Materials and Methods: Mineralogical, chemical, and spectral properties have been conducted on a variety of samples having different formation processes on Mauna Kea Volcano in Hawaii (e.g., [5,6]). We have chosen to characterize the thermal and evolved gas behaviors of a representative suite of samples. A Perkin Elmer DSC-7 differential scanning calorimetry (DSC) was modified to conduct variable-pressure thermal analysis [9]. Platinum ovens were used to heat samples with a temperature ramp rate of 20°C/min with a N₂ carrier gas at 100 torr pressure (which are the operating pressure and carrier gas used by TEGA). Evolved gases from the DSC were characterized by a quadrupole mass spectrometer.

Results and Discussion: The thermal and evolved gas analysis of jarositic tephra material which formed by sulfuric acid HWMK515, hydrothermal alteration of basaltic tephra, is shown in Figure 1. Detailed chemical, mineralogical, spectral, and magnetic properties of the jarositic tephra are provided in Morris et al. [6]. The mineralogy of the sample is dominated by jarosite and plagioclase feldspar. Thermal and evolved gas analysis for the jarositic tephra indicates a strong endoenthalpic 420°C, transition near which marks dehydroxylation of the ferric-OH bonds in jarosite and the evolution of water (e.g., $2KFe_3(SO_4)_2(OH)_6 \rightarrow$ $K_2SO_4 \cdot Fe_2(SO_4)_3 + 2Fe_2O_3 + 6H_2O$). A second endoenthalpic transition near 580°C represents the

breakdown of sulfate in jarosite. During this transformation, K_2SO_4 (and Na_2SO_4) and Fe_2O_3 form as SO_2 is evolved (e.g., K_2SO_4 · $Fe_2(SO_4)_3 \rightarrow K_2SO_4$ + $Fe_2O_3 + 3SO_2 + 3/2O_2$). This sample does not appear to have any phyllosilicates and Fe oxyhydroxides present. The amount of water given off from the sample was about 2 wt. %, which correlates well with the expected amount of water in the surface "soils" and dust on Mars. It also released most of its water around $420^{\circ}C$, which falls within the temperature range (350-500°C) where most of the water was driven off during the pyrolysis of surface materials at the Viking sites. Another interesting analogy of this sample to the Mars surface materials is a sulfur content of 6.46 wt. % SO_3 .

The thermal and evolved gas analysis of palagonitic tephra HWMK602 from near the Very Large Base Array is shown in Figure 2. The palagonitization process has resulted in hydrolytic alteration of tephra rinds to nanophase Fe-oxides and hydrated glass. Water is continuously driven off until 700°C indicating that the water has been structurally incorporated into the glass phase during the palagonitization process. The <1 mm fraction of HWMK602 contains about 3.75 wt.% H₂O [6].

For comparison, the thermal and evolved gas analysis for a relatively unaltered tephra, PH13, from the Puu Huluhulu cinder cone on the saddle between Mauna Kea and Mauna Loa is shown in Figure 3. PH13 consists of unaltered glass and crystalline phases olivine and Fe-Ti spinel. Heat flow illustrates no major endothermic or exothermic events, however, water is driven off from the glass phase between 75 and 300°C. This sample contains 1.29 wt.% water (<1 mm fraction of PH13).

The thermal and evolved gas behaviors of Mars analog materials will provide critical "feed forward" information on the possible mineralogy and chemistry of Mars surface "weathering" phases that will enhance the planning for instruments and investigations on future Mars robotic missions (e.g., 2007 Mars Scout, 2009 Mars Science Laboratory) as well as provide a fundamental understanding of processes for the waterand other volatile-bearing phase on Mars.

References: [1] Biemann K. et al. (1977) J. Geophys. Res. 82, 4641-4658. [2] Boynton W. V. et al. (2002) Science, 297, 81-85. [3] Feldman W. C. et al. (2002) Science, 297, 75-78. [4] Wolfe E. W. et al. (1996) U.S.G.S. Prof. Paper 1557. [5] Morris R. V. et al. (2001) J. Geophys. Res. 106, 5057-5084. [6] Morris R. V. et al. (2000) J. Geophys. Res., 105, 1757-1817. [7] Lauer Jr. H. V. et al. (2000). LPSC XXXI, Abst. # 1990, (CD-ROM). [8] Golden D. C. et al. (1993) J. Geophys. Res., 98, 3401-3411. [9] Golden D. C. et al. (1999) LPSC XXX, Abst. # 2027 (CD-ROM).

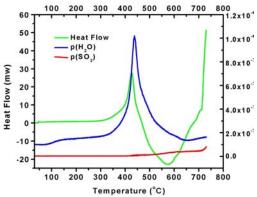


Figure 1. Thermal and evolved gas analysis of jarositic tephra sample HWMK515 from near the summit of Mauna Kea Volcano in Hawaii (DSC baseline correction). This sample displays many of the chemical and volatile characteristics of the Mars "soils" and dust analyzed at the Viking sites.

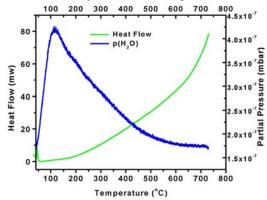


Figure 2. Thermal and evolved gas analysis of palagonitic tephra sample HWMK602 from near the Very Large Based Array on Mauna Kea Volcano in Hawaii (no DSC baseline correction). This sample displays a continuous water loss up to 700°C.

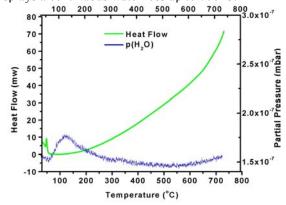


Figure 3. Thermal and evolved gas analysis of unaltered basaltic tephra sample PH13 (no DSC baseline correction). Most of the structurally-bond water in the glass is driven off prior to 300°C.